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The measurement of PM_{2.5}, including semi-volatile components, in the EMPACT program: results from the Salt Lake City Study

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Abstract

The Salt Lake City EPA Environmental Monitoring for Public Access and Community Tracking (EMPACT) project, initiated in October 1999, is designed to evaluate the usefulness of a newly developed real-time continuous monitor (RAMS) for total (non-volatile plus semi-volatile) PM_{2.5} mass and the health relevance of PM_{2.5} measured by this method as compared to other measurements of PM_{2.5} parameters. Ammonium nitrate and semi-volatile organic compounds (SVOC) are significant components of fine particles in many urban atmospheres. These components however, are not properly measured by current EPA accepted methods, such as the PM_{2.5} FRM, due to loss of semi-volatile material (SVM) from the filter during sampling. Continuous PM_{2.5} mass measurements are attempted using methods such as the R&P TEOM monitor. This method however, heats the sample to remove particle-bound water. This results in evaporation of significant amounts of semi-volatile material. Similarly, continuous carbonaceous material monitors are expected to lose semi-volatile organic material during sample collection.

Continuous RAMS and collocated TEOM monitor data have been obtained at the EMPACT sampling site in Salt Lake City, Utah during a 2-year period. Results obtained for the continuous determination of total PM_{2.5} mass with the RAMS have been validated by comparison with results obtained from collocated PC-BOSS diffusion denuder integrated samples at the EMPACT sampling site in Salt Lake City, Utah during three intensive sampling periods (winter 1999–2000, summer 2000, and winter 2000–2001). While the RAMS is shown to measure total PM_{2.5}, including semi-volatile nitrate and organic material, commercially available semi-continuous TEOM and C monitors do not reliably measure these species.

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1. Introduction

Human health endpoints associated with exposure to airborne particulate matter (PM) include increased

mortality and morbidity from respiratory and cardiovascular disease (Schwartz et al., 1996; US EPA, 1996). These effects are observed with exposure to concentrations substantially below the US PM₁₀ ambient air quality standard. The observed exacerbation of health problems is believed to be associated more closely with exposure to fine particles (>2.5 µm) than coarse particles (<2.5 µm). As a result, the US Environmental

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Protection Agency has promulgated revised standards for PM which establishes new annual and 24-h fine PM standards with $PM_{2.5}$, measured according to the Federal Reference Method ($PM_{2.5}$ FRM), as the indicator (Schaefer et al., 1997). This recognition of fine and coarse particles as different classes of PM pollutants is an advance in the understanding and control of PM. However, ambient fine PM is not a single pollutant, but a mixture of many chemical species. Major components include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic and transition metals); organic material; elemental carbon (EC); and crustal components. The mass of stable species such as trace and crustal elements, and ions such as sulfate, can be accurately measured by single filter samplers such as the $PM_{2.5}$ FRM (Musick, 2000; Schaefer et al., 1997) and the Tapered Element Oscillating Microbalance, TEOM (Patashnick and Rupprecht, 1991). However, semi-volatile fine particulate species (SVM) such as ammonium nitrate and organic material are not accurately determined by these techniques (Eatough, 1999; Pang et al., 1999, 2002; Lewtas et al., 2001).

Past toxicological studies of respirable PM have focused on the evaluation of exposure to genotoxic compounds (Hannigan et al., 1994; Lewtas, 1991; MacGregor et al., 1994). The most extensive of these studies have been those conducted under the umbrella of the Integrated Air Cancer Project of EPA (IACP, 1988; Lewtas, 1991). Results of the IACP studies have shown that significant concentrations of both gas and particulate phase mutagens are present in urban atmospheres and that the greatest exposure to these mutagens is associated with the products of photochemistry of NO_x and automotive and wood-smoke emissions (Lewis et al., 1988; Walsh et al., 1993). Nitrated mutagenic compounds are rapidly formed in wood smoke (Kamens et al., 1984, 1985) and automobile emissions (Kleindienst et al., 1992) in the presence of O_3 and NO_2 and a large increase in both gas and particulate phase mutagenicity results from this chemistry (Cupitt et al., 1987, 1988). Because of the potential mutagenicity of secondary semi-volatile organic compounds in urban atmospheres it is important to determine the extent to which these species may contribute to the exacerbation of health effects. However, the accurate assessment of effects associated with exposure to semi-volatile secondary organic compounds will require monitoring techniques for the determination of such compounds in PM (Eatough et al., 1999, 2001; Lewtas et al., 2001).

The objectives of the Salt Lake City EMPACT project (Long et al., 2000) addressed in this paper were: (1) evaluate the RAMS, a newly developed, real-time, continuous monitor for total (including SVC) $PM_{2.5}$ mass. Particular attention was paid to the time- and health-relevance of results obtained with this method, compared to other $PM_{2.5}$ measurements. (2) Compare a

variety of 24-h and continuous $PM_{2.5}$ methods which include the EPA $PM_{2.5}$ FRM (equilibrated mass), TEOM (non-volatile mass), RAMS (total mass), and semi-continuous instruments for measuring EC and organic carbon (OC). The measurement of total $PM_{2.5}$ mass is particularly important in Salt Lake City because present regulations limit wood-burning on “red” episode days and particles from wood smoke have a large semi-volatile component.

2. Experimental methods and procedures

2.1. Sampling site

The EPA EMPACT monitoring site is located immediately adjacent to the State of Utah Air Quality Monitoring site at the Hawthorne Elementary School in Salt Lake City, Utah. The site is in a residential area approximately 4 km southeast of the central business district. The population in Salt Lake Valley is approximately 750,000. $PM_{2.5}$ pollution at the site is expected to be dominated by primary and secondary emissions from mobile sources and, during the winter, wood smoke from home combustion. There are no major point sources which are expected to make a significant impact at the Hawthorne site.

2.2. Sampling methods

2.2.1. $PM_{2.5}$ FRM

The FRM contains a $2.5\ \mu m$ WINS impactor followed by a single filter in a temperature controlled environment. Collected mass is determined gravimetrically. Protocols for pre- and post-equilibration and weighing are well defined (Musick, 2000). The FRM data were obtained by the State of Utah Division of Air Quality with an R&P sequential $PM_{2.5}$ FRM monitor.

2.2.2. R&P TEOM monitor

One-hour-averaged, non-volatile $PM_{2.5}$ mass concentrations were determined using an R&P TEOM monitor operating under normal conditions (Patashnick and Rupprecht, 1991). As stated above, semi-volatile PM will evaporate at the standard operating temperature of the instrument ($50^\circ C$, $30^\circ C$ during winter months), which is required to remove particle-bound water (Mignacca and Stubbs, 1999). This technique measures non-volatile PM.

2.2.3. PC-BOSS

The combination of technology used in the High-Volume Brigham Young University Organic Sampling System (BIG BOSS) (Tang et al., 1994) and the Harvard particle concentrator (Sioutas et al., 1994) has resulted in the Particle Concentrator-Brigham Young University

Organic Sampling System (PC-BOSS) (Ding et al., 2001; Eatough et al., 1999; Lewtas et al., 2001). The configuration and operation of the PC-BOSS as used in the Salt Lake EMPACT program has been previously described (Lewtas et al., 2001).

The PC-BOSS was used for sample collection to determine fine particulate mass, crustal and trace elements, sulfate, carbonaceous material (elemental and organic), nitrate, semi-volatile organic material, and semi-volatile nitrate. Samples for the chemical characterization of PM_{2.5} in the minor flow following a particle concentrator and a BOSS diffusion denuder were collected in a filter pack containing a pre-fired 47 mm quartz filter (Pallflex) followed by 47 mm charcoal impregnated glass fiber filter (CIG, Schleicher and Schuell, Dassel, Germany) to determine fine particulate carbonaceous material and nitrate, including semi-volatile species lost from the particles during sampling. A second parallel filter pack containing a 47 mm Teflon (Whatman) filter followed by a 47 mm Nylon (Gelman, Nylasorb) filter was used to determine PM_{2.5} filter retained (non-volatile) mass, sulfate and nitrate, and any nitrate lost from the particles during sample collection. A side flow filter pack, prior to the particle concentrator, contained a 47 mm polycarbonate (Corning, Nuclepore, 0.4 µm pore size) filter followed by a 47 mm CIG to collect particles (excluding semi-volatile species lost during sampling) and gas phase organic material after the 2.5 µm inlet cut. These data were compared to data from the minor flow filters to determine the particle concentrator efficiency (Ding et al., 2001; Eatough et al., 1999; Lewtas et al., 2001). Twenty-four-hour samples were collected each day during both winter and summer sampling periods for comparison with 24-h averaged RAMS results and equilibrated PM_{2.5} mass concentrations measured on a 24-h basis by the PM_{2.5} FRM.

2.2.4. RAMS

The Real-time total Ambient Mass Sampler (RAMS), based on diffusion denuder, Nafion dryer and TEOM monitor technology, was used for the real-time determination of total PM_{2.5} mass, including semi-volatile species (Eatough et al., 1999, 2001). The RAMS measures total PM_{2.5} mass with a TEOM monitor using a “sandwich” filter to retain SVC which would be lost from particles in a conventional TEOM monitor. The sandwich filter consists of a Teflon-coated particle collection filter (R&P TX40) followed by a charcoal-impregnated glass fiber filter (CIG, Schleicher and Schuell) to collect any semi-volatile compounds lost from the particles during sampling. Care must be taken to remove from the sample stream all gas phase species that can be absorbed by the CIG filter in order to prevent over-determination of PM_{2.5} mass. This is accomplished with a series of denuders to remove gas

phase organic compounds, O₃, NO₂, SO₂ and HNO₃ and two Nafion dryers to remove gas phase water. The configuration and operation of the RAMS as used in the EMPACT study has been previously described (Eatough et al., 1999, 2001; Long et al., 2000, 2001). The configuration includes an active blank sampler to monitor and correct for gas phase compounds not removed before the sandwich filter which can be sampled with the CIG. RAMS data were averaged over 1-h periods throughout the 2 years of the study for comparison with 1-h averaged TEOM data. Twenty-four-hour averaged data were also calculated for comparison with results obtained with the PC-BOSS and PM_{2.5} FRM samplers. Because of the presence of the two Nafion dryers, particle bound water is not measured with the RAMS (Obeidi, 1999).

2.2.5. R&P series 5400 ambient carbon particulate monitor

The Series 5400 Ambient Carbon Particulate Monitor from Rupprecht & Patashnick was used to characterize the total-carbon content of suspended particles on a continuous basis. The Series 5400 performs a thermal-CO₂ analysis to determine the amount of organic and EC present in a collected sample. One hour total-carbon concentration averages were obtained during the winter 1999–2000 and winter 2000–2001 sampling periods, enabling comparison with the 1 h averaged TEOM and RAMS data.

2.2.6. Anderson aethalometer

An Anderson Instruments Inc. (Model RTAA-900) Aethalometer was used for the last 18 months of the study for the determination of aerosol EC on a continuous basis. One hour EC concentration averages were obtained during the summer 2000 sampling period, and compared with the 1 h averaged TEOM and RAMS data.

2.3. Analytical methods

2.3.1. Mettler UMT2 microbalance

A Mettler UMT2 Microbalance was used for the determination of collected fine particle mass on a 47 mm Teflon (Whatman) filter sampled from the PC-BOSS minor flow or the Teflon filter of the PM_{2.5} FRM sampler.

2.3.2. TPV analysis

Temperature Programmed Volatilization (Tang et al., 1994; Ellis and Novakov, 1982) was used in the analysis of collected samples for total carbonaceous material. In this method, the various sample filters are heated from ambient temperature at a predetermined ramp rate to a predetermined termination temperature. The ramp rate and termination temperatures are dependent on the type

of filter being analyzed. Quartz filters are heated to 800°C in an N₂/O₂ atmosphere. Charcoal impregnated filters are heated to 400°C in an N₂ atmosphere. Carbon in compounds desorbed from the filters during the heating process is catalytically converted to CO₂ and detected by non-dispersive infra-red absorption.

2.3.3. Dionex ion chromatograph

A Dionex Model 500 ion chromatograph with a separator column, anion fiber suppressor, and conductivity detector was used for the analysis of collected samples for nitrate and sulfate. Sample filters are ultrasonically extracted and the concentrations of sulfate and nitrate in the various solutions determined by peak area measurement and comparison to standards.

2.3.4. PIXE

Proton Induced X-ray Emission (PIXE) was used for the determination of trace metals on selected samples collected on nuclepore filters in the PC-BOSS side-flow (Mangelson et al., 1979).

3. Results and discussion

3.1. Comparison of RAMS with TEOM monitor results

The 1-h average RAMS and TEOM monitor results obtained during a 2-week period of the winter 1999–2000 study are given in Fig. 1a. This figure illustrates changing PM concentrations over the 2-week period with the formation and break up of a high pressure episode (inversion) over the Salt Lake Valley. RAMS PM_{2.5} mass measurements are generally equal to or greater than the TEOM PM_{2.5} mass measurements preceding, during and following the inversion. During the inversion period, daily trends indicate the presence of late evening and mid-morning PM_{2.5} peaks. Evening peaks can be attributed to the lowering of the inversion height as the temperature drops and also to increased automobile emissions associated with the evening commute. Mid-morning peaks are attributed to automobile emissions from the morning commute. The evening and mid-morning peaks are less evident in the absence of the inversion. For this winter sampling period the RAMS and TEOM PM_{2.5} mass averages were 18.8 and 13.7 µg/m³, respectively.

Fig. 2a contains the 1-h averaged RAMS and TEOM monitor results obtained during a 2-week period of the summer 2000 study. This figure illustrates PM_{2.5} concentrations during a period when most of northern Utah was impacted by smoke generated by wild fires. As in the winter 1999–2000 study period, RAMS PM_{2.5} measurements are equal to or greater than TEOM measurements. The greatest difference between RAMS

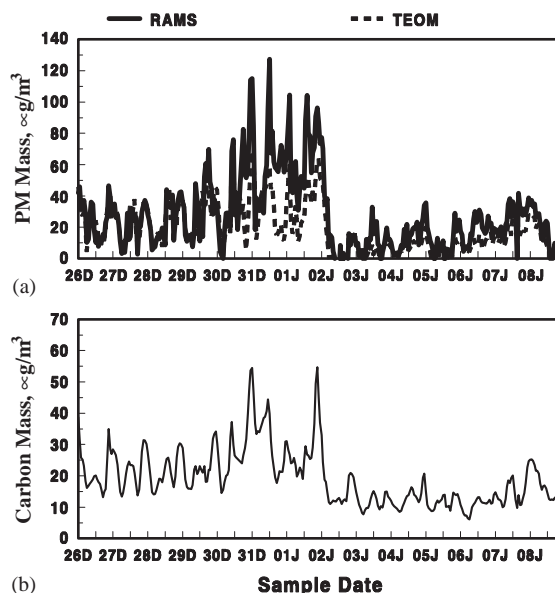


Fig. 1. Comparison of (a) the one-hour average RAMS and TEOM PM_{2.5} mass and (b) R&P Series 5400 Carbon Analyzer total carbon results at the Salt Lake City EMPACT site from 26 December 1999 to 8 January 2000.

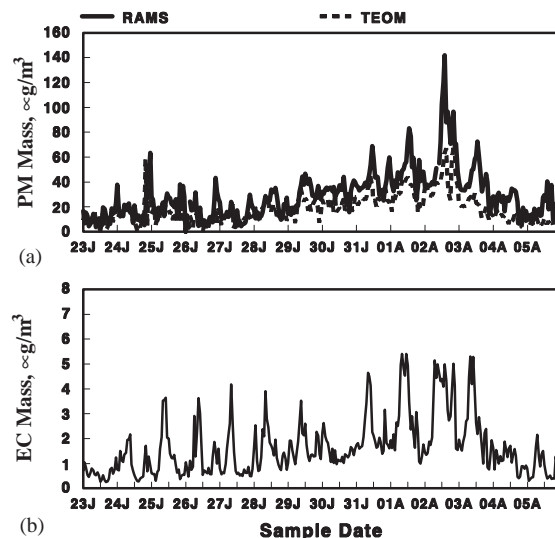


Fig. 2. Comparison of (a) the 1-h average RAMS and TEOM PM_{2.5} mass and (b) Anderson Aethalometer EC results at the Salt Lake City EMPACT site from 23 July 2000 to 5 August 2000. Salt Lake City was impacted by wild fires to the east during 31 July–4 August.

and TEOM measurements is observed over the time period of 31 July–3 August, 2000, when the area was most impacted by the smoke from several forest fires located in the Wasatch Mountains immediately east of the Salt Lake Valley. Daily trends during the forest fire

episode differ from those observed during the winter inversion episode by the presence of a mid-day $\text{PM}_{2.5}$ peak. This peak can be explained by an increased mixing of forest fire generated pollutants in an upper air layer with stagnant valley air during the middle of the day as a result of the break up of the nighttime inversion which allows for more complete mixing of the atmosphere. The same mid-morning and late evening peaks observed during the winter sampling period are visible in the time period preceding the forest fire episode (Fig. 2a). These peaks can also be attributed to “rush-hour” automobile emissions and to the lowering of the inversion height at night. For the summer sampling period, the RAMS and TEOM averages were 16.1 and $11.1 \mu\text{g}/\text{m}^3$, respectively.

The 1-h average RAMS and TEOM monitor results obtained during a 10-day period of the winter 2000–2001 study are given in Fig. 3a. During this 10-day period the Wasatch Front was influenced by a generally persistent high pressure condition, resulting in valley inversions and generally stagnant air conditions. The high pressure was established at the start of the period. The inversion weakened on 29 December, to be reestablished later that day. A weak front passed through the region on 2 January, followed immediately by a persistent inversion until the end of the period. Skies were clear and there was no precipitation throughout the period. The breakdown of the inversion late on 29 December and reformation later that day and the similar change on 2 January are evident in the data. RAMS $\text{PM}_{2.5}$ mass measurements are generally equal to or greater than the TEOM $\text{PM}_{2.5}$ mass measurements preceding, during,

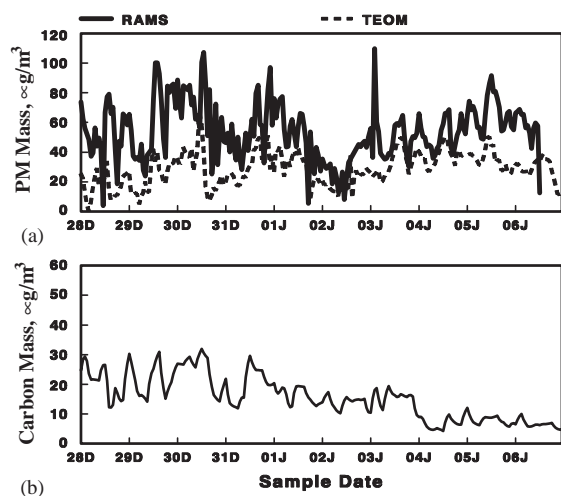


Fig. 3. Comparison of (a) the 1-h average RAMS and TEOM $\text{PM}_{2.5}$ mass, and (b) R&P Series 5400 Carbon Analyzer total carbon results at the Salt Lake City EMPACT site from 28 December 2000 to 6 January 2001.

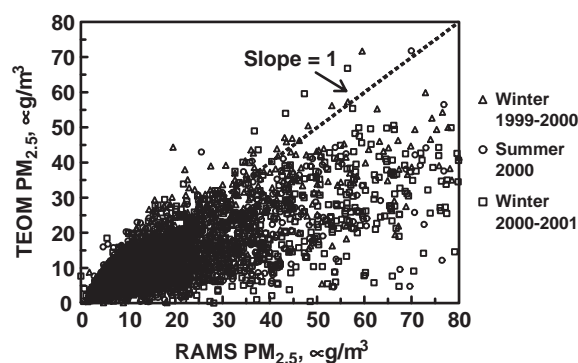


Fig. 4. Comparison of RAMS and TEOM 1-h average $\text{PM}_{2.5}$ samples collected at the Salt Lake City EMPACT site from December 1999 through February 2001.

and following the inversions at the Salt Lake site. Peaks in PM concentrations tend to occur each morning and each evening, similar to those observed during the winter 1999–2000 sampling period. For the winter 2000–2001 sampling period, the RAMS and TEOM averages were 25.5 and $14.6 \mu\text{g}/\text{m}^3$, respectively. On the average, over the three sampling periods of the study, RAMS mass measurements were 34% higher than those obtained with the TEOM monitor. The higher RAMS $\text{PM}_{2.5}$ mass, compared to that of the TEOM monitor can be attributed to the presence of semi-volatile PM which is measured by the RAMS, but not by the TEOM. An x vs. y comparison of the 1-h RAMS and TEOM data for the three study periods is given in Fig. 4. Complete RAMS and TEOM data obtained during the 2 year sampling period are available on the BYU-EMPACT website, <http://empact.byu.edu>.

The linear regression results of RAMS total vs. TEOM non-volatile $\text{PM}_{2.5}$ mass for the data shown in Fig. 4 are given in Table 1. The lack of agreement between the two data sets is reflected in the low values of R^2 for these comparisons and the high values of the bias and σ . The relatively small errors in the last squares calculated slopes is due to the large number of data points included in the regression analyses. The extreme spread in the comparison of the RAMS and TEOM monitor data is due, in part, to the comparison of 1-h average data. This is a short enough time period that data points collected immediately after time periods of very high concentrations of semi-volatile fine particulate material will yield very low TEOM monitor concentrations due to the continued loss of semi-volatile material previously collected (Eatough et al., 1999). This wide variation in the RAMS compared to the TEOM monitor data is much reduced if 24-h averaged data are compared. However, the slope for the comparison of 24-h data is similar to that given in Table 1 for the comparison of 1-h data.

Table 1
Results of the statistical analysis of PM_{2.5} 1- and 24-h samples

<i>x</i> vs. <i>y</i>	<i>n</i>	<i>R</i> ²	Slope ^a	intercept (μg/m ³)	<i>X</i> Average (μg/m ³)	<i>Y</i> Average (μg/m ³)	<i>X</i> – <i>Y</i> Bias (μg/m ³)	<i>σ</i> (μg/m ³)	<i>σ</i> (%)
<i>One-hour samples</i>									
RAMS measured vs. TEOM non-volatile mass	1510 ^b	0.60	0.53±0.01	3.65	18.8	13.7	5.1	6.5	39.8
		0.55	0.64±0.01	0					
	1738 ^c	0.53	0.42±0.01	4.31	16.1	11.1	5.0	5.3	38.6
		0.40	0.59±0.01	0					
	1213 ^d	0.50	0.35±0.01	5.67	25.5	14.6	10.9	9.1	45.1
		0.40	0.48±0.01	0					
4461 ^c		0.53	0.42±0.01	4.74	19.6	13.0	6.6	7.3	45.1
		0.44	0.55±0.00	0					
<i>24-hour samples</i>									
RAMS measured vs. PC-BOSS constructed mass	47 ^b	0.90	0.95±0.05	1.40	17.1	17.7	−0.6	2.7	15.2
		0.90	1.01±0.03	0					
	41 ^c	0.86	0.88±0.06	2.95	14.0	15.2	−1.2	2.2	14.8
		0.82	1.03±0.03	0					
	28 ^d	0.90	0.96±0.06	1.10	29.0	28.9	0.1	3.4	11.9
		0.90	0.99±0.03	0					
116 ^c		0.91	0.94±0.03	1.86	18.7	19.5	−0.7	2.8	14.4
		0.90	1.00±0.02	0					
PC-BOSS total constructed vs. FRM mass	51 ^b	0.94	1.07±0.04	−3.24	18.2	16.2	2.0	1.8	10.7
		0.92	0.94±0.02	0					
	13 ^f	0.89	1.04±0.11	−5.35	11.8	6.9	4.9	NA ^g	
		0.73	0.61±0.04	0					
	41 ^c	0.76	0.48±0.04	−0.09	19.3	9.1	10.2	NA	
		0.76	0.47±0.02	0					
38 ^d		0.83	1.29±0.10	−2.18	24.7	29.8	−5.1	6.0	22.1
		0.83	1.23±0.05	0					
RAMS measured vs. FRM mass	63 ^b	0.75	0.97±0.07	1.07	16.4	14.9	1.5	4.1	26.6
		0.75	0.93±0.04	0					
	23 ^f	0.75	0.70±0.09	2.04	13.8	7.6	6.2	NA	
		0.72	0.57±0.04	0					
	65 ^c	0.87	0.51±0.02	0.93	12.8	7.5	5.3	NA	
		0.72	0.57±0.04	0					
47 ^d		0.74	1.17±0.10	6.00	22.4	32.2	9.8	2.9	10.5
		0.71	1.35±0.06	0					
R&P total carbon vs. PC-BOSS total carbon	51 ^b	0.59	0.53±0.06	2.10	10.8	7.9	2.9	1.8	19.6
		0.53	0.68±0.03	0					
	48 ^c	0.48	0.77±0.12	0.45	11.7	9.5	2.2	2.2	20.9
Aethalometer EC vs. PC-BOSS elemental carbon		0.48	0.81±0.04	0					
	43 ^d	0.75	0.88±0.08	0.13	1.32	1.29	0.02	0.34	26.3
		0.74	0.95±0.05	0					

^aSlopes are given for (1) calculated intercept and (2) zero intercept.

^bData for the Winter 1999–2000 sampling period.

^cData for the Summer 2000 sampling period.

^dData for the Winter 2000–2001 sampling period.

^eData for 1999–2001.

^fData for late Winter 2000.

^gNA, *σ* could not be calculated because the sampler bias was greater than *σ*.

Table 2
Average PM_{2.5} composition during various study periods as collected by the PC-BOSS Sampler, µg/m³

Sampling period	Ammonium sulfate	Non-volatile ammonium nitrate	EC	Non-volatile organic Material	Lost ammonium nitrate	Lost SVOM	Crustal
Winter 1999–2000							
12/31/99–01/18/00	1.5	3.9	1.9	4.9	0.3	3.5	1.3
02/10/00–02/23/00	0.6	1.4	1.0	1.9	0.1	4.0	0.7
Summer 2000	2.5	0.7	1.3	14.5	0.2	4.0	1.7
Winter 2000–2001	4.2	6.7	1.6	12.2	1.9	2.9	1.5

3.2. Comparison of PC-BOSS with RAMS results

Integrated PC-BOSS samples were used to determine the mass of PM_{2.5} including material retained on a filter and semi-volatile nitrate and organic material lost from the filter during sampling. Due to the Salt Lake atmosphere containing excess ammonia, PC-BOSS sulfate and nitrate were assumed to be present as ammonium sulfate and ammonium nitrate, respectively. It was assumed that fine particulate organic material was 61% carbon, typical of an aged urban aerosol (Turpin and Lim, 2001). However, during the sampling period impacted by fresh smoke from the forest fires, organic material was assumed to be 71% carbon, more typical of a young aerosol (Turpin and Lim, 2001; Eldred et al., 1990; Malm et al., 1994). Crustal material was estimated from the PIXE results for Al and Si and the crustal averages for these elements. Generally, crustal material mass determined by the PC-BOSS is 10% of the non-volatile mass measured by the TEOM monitor. Therefore, crustal mass is also estimated where not available as 10% of the non-volatile mass measured by the TEOM monitor. Constructed mass, obtained for each PC-BOSS sample, was calculated as the sum of crustal material estimated from the Al and Si concentrations, ammonium sulfate obtained from sulfate on the Teflon filters, ammonium nitrate from the nitrate on Teflon filters, the volatile ammonium nitrate from the nitrate on the Nylon filters, the EC collected on the quartz filters, and the total organic carbonaceous material which is the sum of the organic material on the quartz filter and the semi-volatile organic material lost from the particles during sampling but collected on the charcoal impregnated glass fiber filter. PC-BOSS constructed mass does not include any particle bound water. The precision of the PC-BOSS data (Ding et al., 2001; Lewtas et al., 2001; Long et al., 2001; Pang et al., 1999) has been shown to be ± 5 –8% for the various measured components, resulting in an over-all precision in the constructed PM_{2.5} of ± 10 –15%. This includes the precision of the particle concentrator efficiency, flow data and analysis results.

Average PM_{2.5} compositions during various study periods are given in Table 2. Because the PC-BOSS denuder sampler has been shown to correctly measure both non-volatile and semi-volatile components of fine PM (Eatough, 1999; Lewtas et al., 2001; Pang et al., 1999), the PC-BOSS constructed mass results were taken as a correct measure of total fine particulate mass. It should be noted that this mass does not include water. The results obtained by the RAMS for the continuous determination of PM_{2.5} mass, including semi-volatile particulate material were averaged (24-h) over the three sampling periods. These results were validated by comparison with results obtained from the PC-BOSS sampler over the same time periods. The linear regression of RAMS measured vs. PC-BOSS constructed PM_{2.5} mass results for the winter 1999–2000 and summer 2000 sampling periods gives $R^2 = 0.90$ ($n = 47$) with a zero intercept slope of 1.01 ± 0.03 , and $R^2 = 0.82$ ($n = 41$) with a zero intercept slope of 1.03 ± 0.04 , respectively (Table 1). For the winter 2000–2001 sampling period linear regression results of RAMS measured vs. PC-BOSS constructed mass give $R^2 = 0.90$ ($n = 28$) with a zero intercept slope of 0.99 ± 0.03 (Table 1). Fig. 5 contains an x vs. y comparison of the RAMS and PC-BOSS results obtained from the three sampling periods. For the combined data shown in Fig. 5, linear regression results give $R^2 = 0.90$ and a zero intercept slope of 1.00 ± 0.02 . Results obtained with the RAMS and the PC-BOSS show that PM_{2.5} mass, excluding water but including other semi-volatile species, can be continuously and accurately monitored at the EPA EMPACT sampling site in Salt Lake City with the RAMS.

3.3. Comparison of PC-BOSS with FRM results

The linear regression of PC-BOSS constructed PM_{2.5} mass vs. PM_{2.5} FRM mass results for the various sampling periods are given in Table 1. For the winter 1999–2000 sampling period, FRM mass results were comparable to those obtained by the PC-BOSS with mass averages of 18.2 and 16.2 µg/m³ for the PC-BOSS

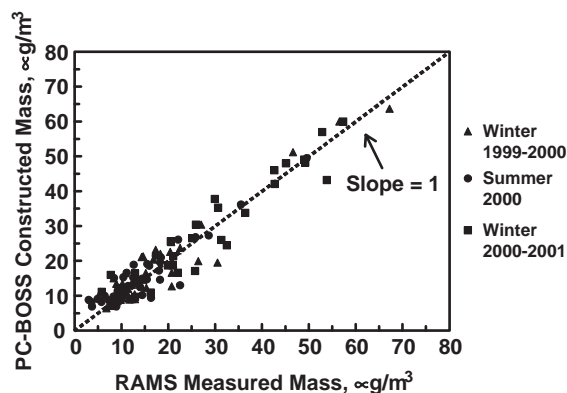


Fig. 5. Comparison of RAMS measured and PC-BOSS constructed $\text{PM}_{2.5}$ for samples collected at the Salt Lake City EMPACT site from December 1999 through February 2001.

and FRM, respectively (Fig. 6, open triangles). However, during the winter 2000–2001 sampling period, the FRM results were frequently higher than those obtained by the PC-BOSS (Fig. 6, open squares). The average PC-BOSS and FRM mass was 24.7 and $29.8 \mu\text{g}/\text{m}^3$, respectively, during this sampling period. Linear regression of the PC-BOSS total vs. FRM mass results give $R^2 = 0.94$ ($n = 51$) and a zero intercept slope of 0.94 ± 0.02 for the winter 1999–2000 sampling period. For the winter 2000–2001 sampling period, linear regression results of the PC-BOSS total vs. FRM mass give $R^2 = 0.83$ ($n = 38$) and a slope of 1.23 ± 0.05 . The higher mass results obtained by the $\text{PM}_{2.5}$ FRM can be attributed to the cold, humid meteorological conditions that existed in the Salt Lake area during the 2000–2001 winter months. During this period, the average daily relative humidity values approached 100% and the average daily temperatures were consistently below freezing (NOAA, 2001). These conditions tend to stabilize semi-volatile species and may also result in significant amounts of water being associated with the particles. The FRM Teflon filter substrate is equilibrated for 24 h to remove this particle bound water. However, a significant amount of water can remain associated with the particles after equilibration. The mass results obtained from the PC-BOSS are constructed by summing the individual chemical components but do not include particle-bound water which is not easily measured. Therefore, the mass obtained by the PC-BOSS represents the non-water $\text{PM}_{2.5}$ mass only whereas the FRM mass may have contributions from particle-bound water. Similar results are obtained by the PC-BOSS and $\text{PM}_{2.5}$ FRM (winter 1999–2000) when relative humidity values are in the 70–90% range. During the later part of the winter 1999–2000 (10–23 February 2000) and throughout the summer 2000 sampling periods, PC-BOSS mass measurements were

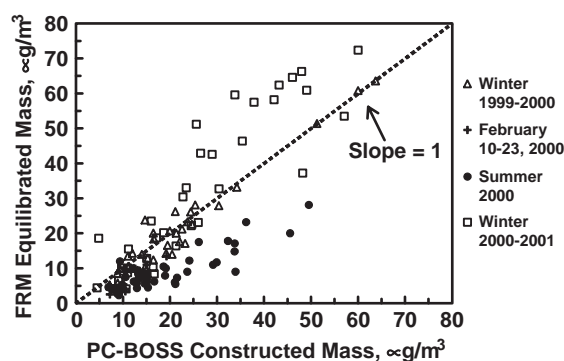


Fig. 6. Comparison of PC-BOSS constructed and FRM equilibrated $\text{PM}_{2.5}$ mass for samples collected at the Salt Lake City EMPACT site from December 1999 through February 2001.

higher than those obtained by the FRM (Fig. 6, plus signs and closed circles, respectively). The PC-BOSS and FRM mass averages for the late winter and summer sampling periods are 11.8 and $6.9 \mu\text{g}/\text{m}^3$ and 19.3 and $9.1 \mu\text{g}/\text{m}^3$, respectively. These time periods were dominated by warmer ($T > 5^\circ\text{C}$) and drier ($\text{RH} < 60\%$) weather conditions, resulting in less retention of water by $\text{PM}_{2.5}$ during the mass equilibration period and a larger contribution by semi-volatile species to total $\text{PM}_{2.5}$ mass (Table 2). Linear regression of the PC-BOSS vs. FRM results for the late winter and summer sampling periods give $R^2 = 0.73$ ($n = 13$) with a zero intercept slope of 0.61 ± 0.04 and $R^2 = 0.76$ ($n = 41$) with a zero intercept slope of 0.47 ± 0.02 , respectively (Table 1). During these two time periods significant SVM is lost from the Teflon filter of the $\text{PM}_{2.5}$ FRM.

3.4. Comparison of RAMS with FRM results

The results obtained by the RAMS for the continuous determination of $\text{PM}_{2.5}$ mass, including semi-volatile particulate material were averaged (24-h) over the various sampling periods. These results were then compared with results obtained from the FRM. The RAMS and FRM mass averages for the winter 1999–2000 sampling period were 16.4 and $14.9 \mu\text{g}/\text{m}^3$. The RAMS measurements were slightly higher than the FRM mass during this time period while the PC-BOSS results were slightly lower. The differences, however, are comparable to the uncertainty in the RAMS and PC-BOSS data of $\pm 2 \mu\text{g}/\text{m}^3$, Table 1. The agreement of the RAMS, PC-BOSS and FRM measurements indicated there was little loss of SVM from the FRM filter as a result of the meteorological conditions (cold and humid). RAMS and FRM mass averages for the winter 2000–2001 sampling period were 22.4 and $32.2 \mu\text{g}/\text{m}^3$.

The FRM measurements were noticeably higher during this sampling period time period due to the decreased mass contribution of semi-volatile material and large contribution by water during this (cold and humid) period. RAMS and FRM mass averages for the later part of the winter 1999–2000 and summer 2000 sampling periods were 13.8 and 7.6 $\mu\text{g}/\text{m}^3$ and 12.8 and 7.5 $\mu\text{g}/\text{m}^3$, respectively. The higher mass measurements obtained by the RAMS during this time period can be attributed to the significant presence of semi-volatile species that are measured by the RAMS but not by the FRM at lower humidity and higher temperatures and also to the decreased contribution of particle-bound water due to the warmer, drier meteorological conditions. The linear regression results of RAMS vs. FRM mass are given in Table 1.

3.5. R&P series 5400 carbon analyzer results

The 1-h average total carbon results obtained from the R&P Series 5400 Carbon Analyzer during a 2-week period from the winter 1999–2000 study are given in Fig. 1b. Comparison of the carbon results in Fig. 1b with the TEOM and RAMS results in Fig. 1a show general agreement with respect to the daily trends in the $\text{PM}_{2.5}$ measurements obtained from the individual monitors. Similarly, the 1-h average total carbon results from the winter 2000–2001 study (Fig. 3b) tend to agree with the TEOM and RAMS results in Fig. 3a with respect to the daily trends in the $\text{PM}_{2.5}$ concentrations.

The results obtained by the R&P Series 5400 Carbon Analyzer for the continuous determination of particulate carbon were averaged (24-h) for comparison with carbon results obtained from the PC-BOSS sampler quartz and CIG filters over the same time periods. During the winter 1999–2000 sampling period, the R&P and PC-BOSS total carbon results averaged 10.8 and 7.9 $\mu\text{g}/\text{m}^3$, respectively. The higher carbon results obtained by the R&P instrument during this winter period are most likely due to interference by gas phase organic compounds which are not measured by the PC-BOSS sampler. The linear regression of R&P measured total carbon vs. PC-BOSS total carbon (non-volatile organic carbon + EC + SVOC) results for the winter 1999–2000 sampling period gives $R^2 = 0.53$ ($n = 51$) with a zero intercept slope of 0.68 ± 0.03 (Table 1). For the summer 2000 sampling period, the R&P and PC-BOSS total carbon results averaged 11.7 and 9.5 $\mu\text{g}/\text{m}^3$, respectively, similar to the winter 1999–2000 study. The linear regression of R&P measured total carbon vs. PC-BOSS total carbon (non-volatile organic carbon + EC + SVOC) results for the summer 2000 sampling period gives $R^2 = 0.48$ ($n = 48$) with a zero intercept slope of 0.81 ± 0.04 (Table 1).

3.6. Anderson aethalometer results

The 1-h average EC results obtained from the Anderson Aethalometer during a 2-week period from the summer 2000 study are given in Fig. 2b. Comparison of the carbon results in Fig. 2b with the TEOM and RAMS results in Fig. 2a show general agreement with respect to the daily trends in the $\text{PM}_{2.5}$ measurements obtained from the individual monitors. This agreement is particularly evident during the time period impacted by the forest fire smoke (31 July–3 August, see Fig. 2).

The results obtained by the Anderson Aethalometer for the continuous determination of EC were averaged (24-h) for comparison with EC results obtained from the PC-BOSS sampler quartz filter over the same time periods. The linear regression of Aethalometer measured EC vs. PC-BOSS EC results for the winter 2000–2001 sampling period give $R^2 = 0.74$ ($n = 43$) with a zero intercept slope of 0.95 ± 0.05 (Table 1). Results obtained with the Aethalometer and the PC-BOSS show that EC determined on a continuous and integrated basis at the EPA EMPACT sampling site in Salt Lake City agreed.

4. Summary

The real-time total ambient mass sampler (RAMS) can be used to accurately and continuously measure $\text{PM}_{2.5}$ mass, including semi-volatile material. The PC-BOSS has proven suitable for the determination of $\text{PM}_{2.5}$ mass and composition, including semi-volatile material, for daily (24-h) sampling periods. Studies have also indicated that the PC-BOSS is capable of $\text{PM}_{2.5}$ mass determination for hourly sampling periods (Ea-tough et al., 1999). Single filter samplers such as the FRM and the TEOM monitor can under-measure $\text{PM}_{2.5}$ mass by as much as 31% for samples collected during the winter study and 42% for samples collected during the summer study. Similarly, samplers such as the R&P carbon monitor do not accurately measure semi-volatile carbonaceous material. The FRM tends to under measure $\text{PM}_{2.5}$ only during warm dry periods while the TEOM monitor consistently under-measures $\text{PM}_{2.5}$ because of loss of SVM from the heated TEOM monitor filter. In cold, damp conditions, the $\text{PM}_{2.5}$ FRM may measure higher suspended $\text{PM}_{2.5}$ mass due to the inclusion of particle-bound water even after the 24-h equilibration period. SVM is a significant component of fine particulate material during summer and winter periods. The accurate determination of $\text{PM}_{2.5}$ mass, including semi-volatile material, on a continuous basis using the RAMS as well as short-term integrated determination of $\text{PM}_{2.5}$ mass and chemical composition with the PC-BOSS, when combined with other monitoring methods currently being used in the Salt Lake City EMPACT program, will provide previously unavailable

information on the composition and concentration of PM suspended in the atmosphere. This information, by providing a more complete description of the exposure component for health studies, should provide a better understanding of health relevant parameters associated with exposure to fine particles.

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